
Influence of some additives on Cu layer formation in underpotential and overpotential regions in acidic CuSO_4 solutions

6. Cu UPD on polycrystalline Pt electrode modified by chemisorbed selenium

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The underpotential deposition (UPD) of copper onto a selenium-modified smooth polycrystalline Pt electrode in acidic CuSO_4 solution was investigated using cyclic voltammetry. The specific pattern of the Cu UPD observed for a clean Pt electrode disappears and a new current peak at potentials (E) much closer to the bulk Cu deposition is formed. This feature of a cyclic voltammogram is similar to that observed earlier for an initially clean Pt electrode in acidic CuSO_4 solutions containing selenite and to that described for an in advance sulphur-modified Pt electrode in an additive-free CuSO_4 solution. The model of copper deposition taking place on two active platinum surface domains, namely, on the free Pt sites and on the selenium-covered ones, was proposed.

Key words: copper, platinum electrode, selenium-modified electrode, underpotential deposition, sulphate solution

INTRODUCTION

Much research has been recently carried out using modified electrodes in various electrochemical systems. The different aspects of the modification of metal electrodes by adatoms and the application of modified electrodes are described in the review works [1–7].

In this regard the adatoms of selenium play an important role [3–6, 8–26]. In addition, some Se substances are known to exert a considerable effect on the acceleration of Cu electrodeposition from acidic CuSO_4 solutions [27–35]. The Cu UPD onto a smooth polycrystalline Pt electrode from acidic CuSO_4 solutions in the presence of selenite was also started to be examined [36–38].

Despite extensive studies devoted to the application of selenium-modified noble metal electrodes, e.g., platinum, for different redox reactions, to our knowledge, the Cu UPD onto a metallic substrate modified by selenium has received less, if any, attention. Therefore, continuing our studies on the Cu UPD onto a modified polycrystalline Pt electrode (the results obtained with the use of the sulphur-modified polycrystalline electrode in acidic CuSO_4 solution were described in [39]), it is of interest to

extend the investigation of such a kind, using Pt electrodes which were subjected to a certain chemical modification.

The aim of this work was to study the UPD of copper from acidic CuSO_4 solution onto a polycrystalline Pt electrode modified by selenium.

EXPERIMENTAL

The working solution used was CuSO_4 0.001 + H_2SO_4 0.5 M. The electrolyte was prepared from doubly distilled water, salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fluka) preheated at 400 °C for 4 h and highest purity H_2SO_4 (Russia). Analytical grade H_2SeO_3 recrystallized additionally was used for the preparation of solutions applied to modify the electrode. Prior to each experiment the working solution was deaerated with Ar gas for 0.5 h.

All experiments were carried out at 20 ± 0.1 °C in a three-electrode thermostated electrochemical cell. The working electrode was a vertical disc with a diameter of 105.5 mm made from a polycrystalline Pt foil (99.99% purity). The counter electrode was a Pt sheet of ca. 4 cm² in area. The reference electrode was a Ag/AgCl/KCl(sat.) electrode. In the

text, all potentials (E) are recalculated with respect to the standard hydrogen electrode (SHE).

The real electrode surface was determined from a hydrogen adsorption voltammetric i/E profile recorded at 100 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ solution, taking a specific charge of $210 \text{ } \mu\text{C}$ for the complete coverage of 1 cm^2 of polycrystalline Pt by adsorbed hydrogen, as reported in [40]. The roughness factor (f) was obtained to be 2.35 ± 0.05 . All currents (i) in the text are recorded as current densities (i_c or i_a) with respect to the geometric area of the electrode.

The pretreatment of the working electrode prior to modification was described elsewhere [38]. The modification of platinum electrode by selenium was made by adsorption of selenium compound at open-circuit potential (OCP) in aqueous H_2SeO_3 solution of different concentration (c) for different time (t_{imm}), following the procedure described in [41]. For each c and also for each t_{imm} triplicate experiments were made. The other specific conditions of modification will be given in an appropriate place of the text or in Figures. The characterization of the modified Pt electrode was carried out by cyclic voltammetry (CV) in $0.5 \text{ M H}_2\text{SO}_4$ solution through a decrease of the charge for hydrogen adsorption. As in the case of a sulphur-modified Pt electrode [39], the degree of coverage by selenium (θ_{Se}) was evaluated from the ratio of $(Q_{\text{H,c}}^{\circ} - Q_{\text{H,c}}^{\text{Se}})/(Q_{\text{H,c}}^{\circ} - Q_{\text{H,c}}^*)$, where $Q_{\text{H,c}}^{\circ}$, $Q_{\text{H,c}}^{\text{Se}}$ and $Q_{\text{H,c}}^*$ are the quantities of electricity associated with the adsorption of hydrogen in the absence of adsorbed selenium, in its presence and under the complete formation of the selenium adlayer, respectively. In particular, the values of θ_{Se} were obtained to be equal to 0.31, 0.33, 0.38 or 0.51 when the selenization of Pt electrode was carried out for 0.5 min in solution containing 0.1, 0.5, 2.0 or 100 mM H_2SeO_3 , respectively.

The transfer of the selenium-modified Pt electrode to another cell for electrochemical measurements was performed without rinsing, *i.e.* under protection of a droplet of solution (the loss of adspecies was not evaluated). The electrode was allowed to stand at OCP for 3 min, and then E cycling started, first toward the negative values. Successive scans were performed until a stationary shape of CVs was recorded (no more than 20 sweeps). In separate experiments, the effect of repetitive triangular potential cycling was also monitored.

In the experiments designed to check whether selenium remains onto a surface of the working electrode after electrochemical measurements in $\text{H}_2\text{SO}_4 + \text{CuSO}_4$ solution, the potential cycling was

stopped at a respective anodic limit, then the electrode was put into pure $0.5 \text{ M H}_2\text{SO}_4$ solution and the i/E curve was recorded at 50 mV s^{-1} . In such a manner, the stability of the selenium adlayer can be characterized and the potential range which assures this stability can be evaluated. It was shown, in particular, that the Se adlayer onto Pt remained actually unaffected if $E_{\text{s,a}}$ did not exceed $+1.0 \text{ V}$.

Cyclic voltammetry was performed using a PI 50-1 potentiostat, a PR-8 programmer and an LKD-003 X-Y recorder (all made in Belarus).

The Nernstian potential (E_{eq}) for Cu/Cu^{2+} couple was estimated by measuring an open-circuit potential of Cu in the $0.5 \text{ M H}_2\text{SO}_4 + 1 \cdot 10^{-3} \text{ M CuSO}_4$ solution and was found to be equal to $+0.243 \text{ V}$.

RESULTS

A series of 8 voltammetric i/E profiles for a bare Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ solution taken from the same cathodic limit $E_{\text{s,c}} = +0.05 \text{ V}$ successively to various anodic limits $E_{\text{s,a}}$ in 0.1 V increments are shown in Fig. 1a. These i/E profiles were recorded after a repetitive cycling between $E_{\text{s,c}} = +0.05 \text{ V}$ and $E_{\text{s,a}} = +1.50 \text{ V}$ to attain the steady-state run of CVs. The general run of the CVs here is quite similar to that reported elsewhere [42]. The set of CVs in Fig. 1a serves for a comparison when the selenium-modified Pt electrode is used for electrochemical measurements.

The stabilized potentiodynamic i/E profiles recorded to $+1.20 \text{ V}$ (Fig. 1b) and lower potential (Fig. 1c) in $0.5 \text{ M H}_2\text{SO}_4$ solution for a Pt electrode modified by selenium in solutions of different concentration of H_2SeO_3 show that the form of CVs changes progressively. When the electrode potential E is cycled in a more narrow interval, the inhibiting effect of selenium on both the hydrogen adsorption/desorption and the formation of platinum surface oxide processes becomes more noticeable. A significant diminution of the electric charge involved in the hydrogen adsorption below $+0.30 \text{ V}$ jointly with the blocking effect on platinum surface oxidation above *ca.* $+0.80 \text{ V}$ (*cf.* Fig. 1c) are the main features at first sight. It was also established that if the upper potential limit is controlled (actual limits in Fig. 1b,c), the stabilized CVs are quite stable and reproducible, thus showing that under these experimental conditions the selenium redox process does not lead to the formation of soluble selenium species. These observations agree well with those reported earlier [20, 36, 38, 41, 43]. Therefore, we have not

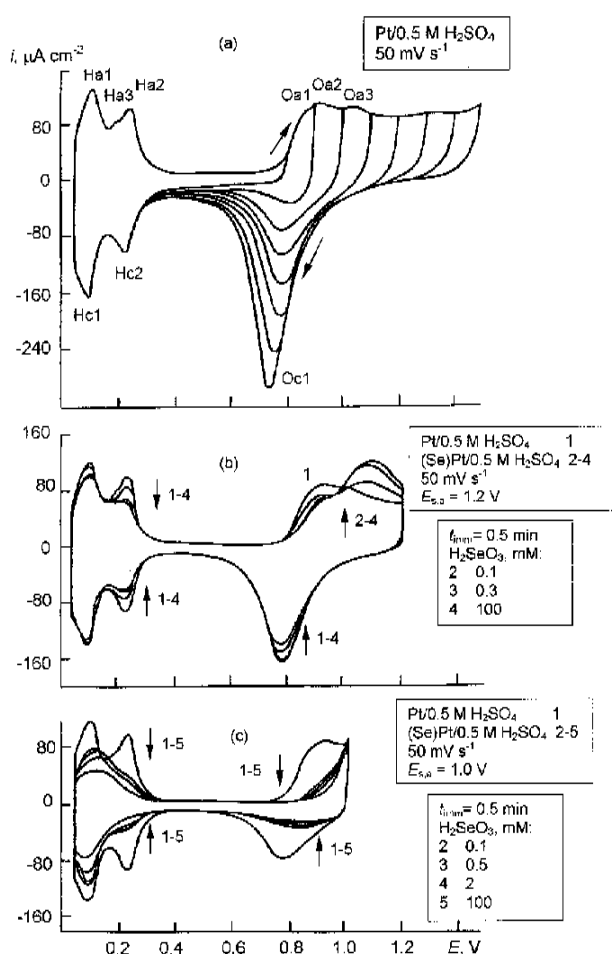


Fig. 1. (a) Potentiodynamic profiles for a bare Pt electrode in 0.5 M H₂SO₄ recorded at 50 mV s⁻¹ from the same cathodic limit $E_{s,c} = +0.05$ V successively to various anodic limits $E_{s,a}$ in 0.1 V increments (in all cases i/E curves were registered after a repetitive cycling between +0.05 and +1.50 V to attain the stabilized run of curves); (b) and (c) stabilized potentiodynamic profiles for Pt (curves 1) or Se-modified Pt (curves 2-5) taken from +0.05 V to $E_{s,a} = +1.20$ V (b) or +1.00 V (c). Conditions of modification are shown in b, c

gone into details of analysing the CVs presented here.

Figure 2 shows the variation in the shape of the stabilized i/E profile in 0.5 M H₂SO₄ + 1·10⁻³ M CuSO₄ solution depending on the value of anodic sweep limit for the bare Pt electrode (Fig. 2a) and for the selenium-modified Pt electrode prepared in solutions of different H₂SeO₃ concentration (Fig. 2b, c). As in the case of the pure H₂SO₄ solution (Fig. 1), the stabilized CVs exhibit certain changes in their profile with increasing $E_{s,a}$. The voltammetric profiles obtained for the bare polycrystalline Pt electrode (Fig. 2a) in Cu²⁺-containing sulphate solution during the negative-going sweep are in principle consistent with those recorded for the same electrode in H₂SO₄

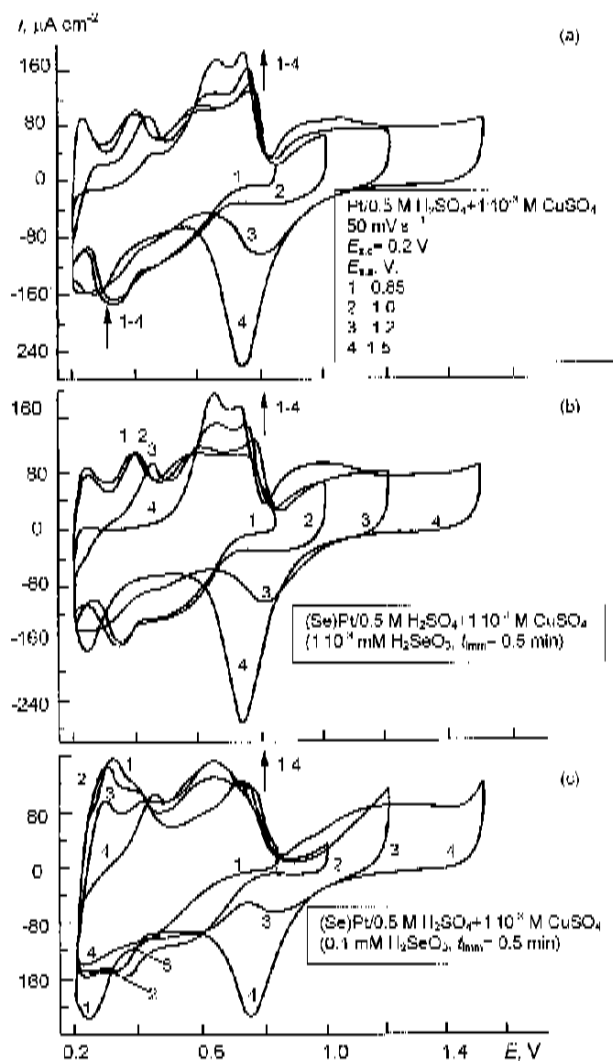


Fig. 2. Stabilized potentiodynamic profiles for a bare Pt electrode (a) or for a Se-modified Pt electrode (b, c) in 0.5 M H₂SO₄ + 1·10⁻³ M CuSO₄ solution recorded at 50 mV s⁻¹ from $E_{s,c} = +0.20$ V successively to various $E_{s,a}$. Conditions of modification are shown in b, c

solution without Cu²⁺ ions (Fig. 1a), naturally with consideration of typical features of the Cu UPD [38, 44, 45]. In particular, a current peak at ca. +0.75 V which corresponds to the reduction of surface platinum oxide (cf. Fig. 1a, peak Oc1) can be observed in the negative E sweep. In the range of ca. +0.70 ... +0.25 V, the broad and complex current peak implying several contributions is distinguished, in agreement with previous studies of the Cu UPD [38, 44, 45].

When a Se-modified Pt electrode was used for the CV, it was obtained that “selenization” in a solution of low concentration of H₂SeO₃ left the negative-going voltammetric profiles practically unaffected (Fig. 2b). As should be expected, the effect of modification was shown to increase with increasing the c of H₂SeO₃ in the solution used for the modi-

fication (Fig. 2c), especially at cycling in the E range which is characteristic of the Cu UPD onto polycrystalline Pt [38, 44, 45]. In this case, the specific pattern of the Cu UPD [38, 44, 45] was somewhat changed and a new current peak at E much closer to the bulk Cu deposition was formed, e.g., the current peak at +0.25 V (Fig. 2c, curve 1). It should be noted that a similar phenomenon has been observed for a sulphur-modified Pt electrode as well [45]. In addition, there is a rather good parallelism between the voltammetric data here for the selenium-modified electrode and those for sulphur-modified Pt electrode [45] or for an initially bare Pt electrode in acidic CuSO_4 solutions with H_2SeO_3 [36, 38], sulphite [39] or other S-containing additives such as thiourea [46], 4,7-dithiadecyl-1,10-disodiumsulphate [46], *cis*-1,2-dicyanoethylene-1,2-dithiolate [47], etc.

It is interesting to note that there are also some formally similar examples related to the UPD of other metals under a strong influence of anion ad-

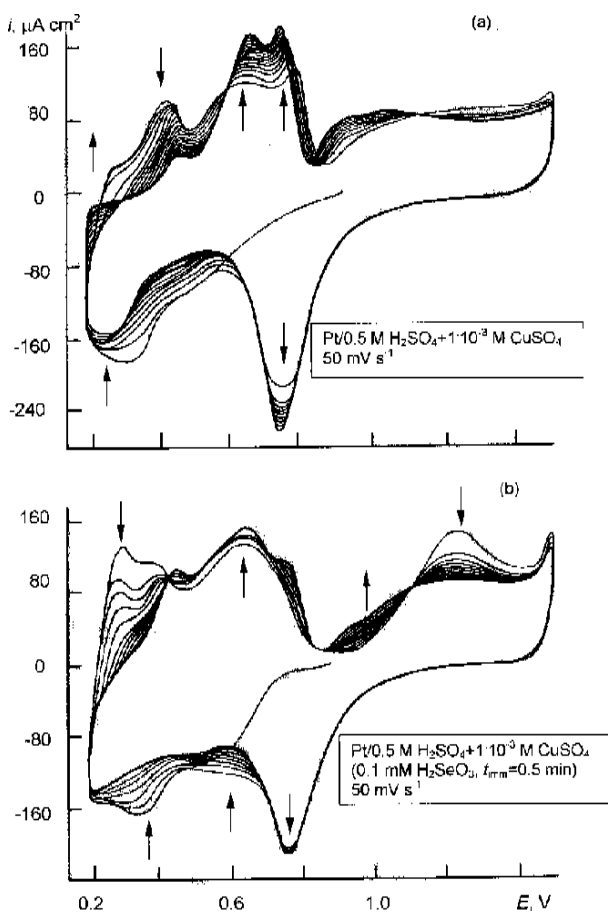


Fig. 3. Repetitive potentiodynamic profiles for a bare Pt electrode (a) or for a Se-modified Pt electrode (b) in $0.5 \text{ M H}_2\text{SO}_4 + 1 \cdot 10^{-3} \text{ M CuSO}_4$ solution recorded at 50 mV s^{-1} between $E_{\text{s,c}} = +0.20$ and $E_{\text{s,a}} = +1.50$ V. Conditions of modification are shown in b. Arrows show the direction of a change of current peaks with a number of successive cycles

sorption [1]. In particular, it has been reported that, in the case of the Ag UPD on Au in solutions of various Cl^- concentrations, besides a slight retardation of the beginning of Ag adsorption at higher positive E , a new rather sharp peak was observed with increasing the Cl^- concentration [48].

In order to obtain an additional information on the experimental conditions allowing the selenium adsorbate to be more stable, the effect of continuous cycling sweeps to different $E_{\text{s,a}}$ on the voltammetric shape of a selenium-modified Pt electrode was investigated. Figures 3 and 4 show the typical sets of CVs recorded at successive cycling, when the upper limit was decreased stepwise from +1.50 to +0.85 V. Some findings are worth noting. Firstly, the sensitivity of cathodic i/E profiles to the number of cycles (n) was recognized to become much stronger, as the upper limit of sweeps was increased. The same is true of the anodic half-cycles. Furthermore, when the electrode potential was cycled within the widest interval (Fig. 3 a, b), resolution of individual waves on the i/E curves became poorer with increasing n , and the attained stationary voltammetric responses for bare Pt and selenium-modified Pt were rather similar in shape. This can suggest that the oxidized form of selenium partially desorbs from the electrode surface in the most posi-

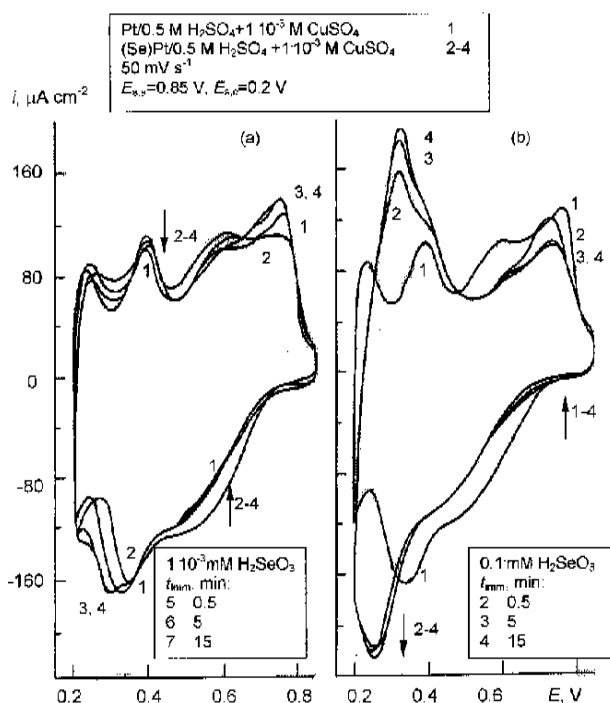


Fig. 4. Repetitive potentiodynamic profiles for a Se-modified Pt electrode in $0.5 \text{ M H}_2\text{SO}_4 + 1 \cdot 10^{-3} \text{ M CuSO}_4$ solution recorded at 50 mV s^{-1} between $E_{\text{s,c}} = +0.20$ and $E_{\text{s,a}} = +1.20$ (a) or $+0.85$ V (b). Conditions of modification are shown in b. Arrows show the direction of a change of current peaks with a number of successive cycles

tive E range, in agreement with the consideration in [14]. Finally, for both the 1st cycle and any of the

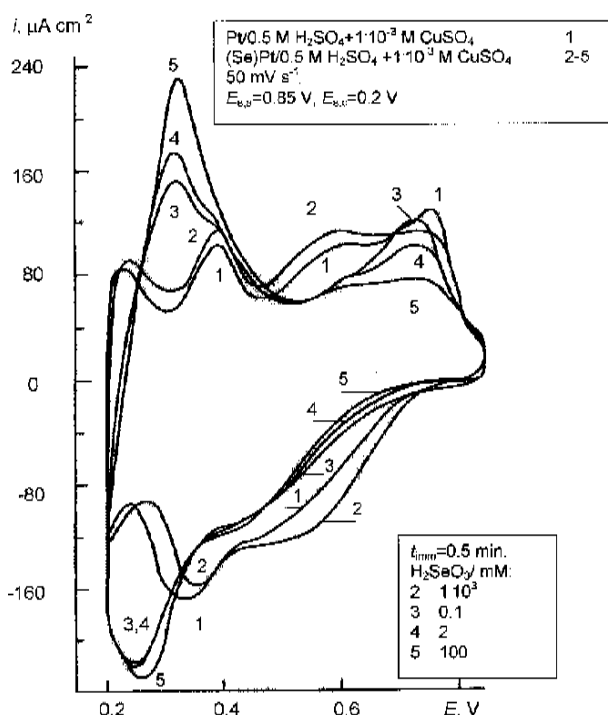


Fig. 5. Stabilized potentiodynamic profiles for a bare Pt electrode (1) or for a Se-modified Pt electrode (2–5) recorded in $0.5 \text{ M H}_2\text{SO}_4 + 1 \cdot 10^{-3} \text{ M CuSO}_4$ solution at 50 mV s^{-1} between $E_{s,c} = +0.20$ and $E_{s,a} = +0.85 \text{ V}$. Modification was performed in solution with different concentrations of H_2SeO_3

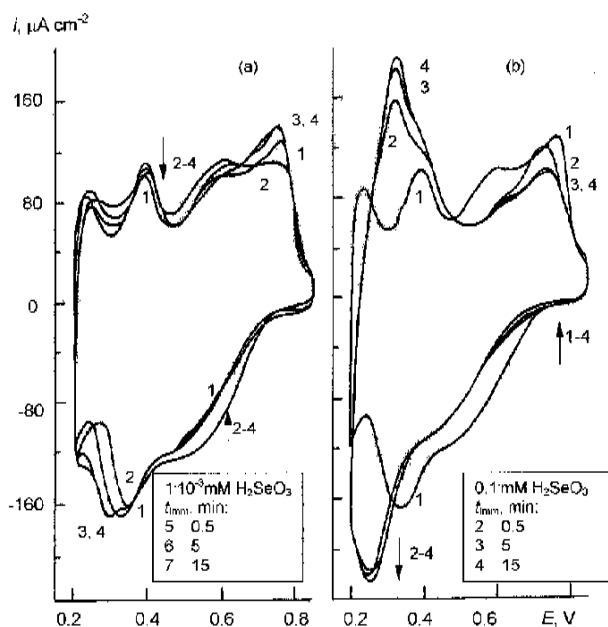


Fig. 6. Stabilized potentiodynamic profiles for a bare Pt electrode (1) or for a Se-modified Pt electrode (2–4) recorded in $0.5 \text{ M H}_2\text{SO}_4 + 1 \cdot 10^{-3} \text{ M CuSO}_4$ solution at 50 mV s^{-1} between $E_{s,c} = +0.20$ and $E_{s,a} = +0.85 \text{ V}$. Modification was performed in aqueous $1 \cdot 10^{-3}$ (a) or 0.1 mM (b) H_2SeO_3 solution for different immersion time t_{imm}

following cycles, the complete i/E profiles are asymmetric with respect to the potential axis suggesting the irreversibility of the process under study. Conversely, the new cathodic current peak and its counterpeak (Fig. 5, 6) seem to approach the pair of reversible peaks related to the UPD/stripping, since the peak potential separation is close to 60 mV for the differently prepared electrodes and the peaks' height ratio i_{pc}/i_{pa} approaches unity with increasing θ_{Se} (cf. Fig. 5, curve 5).

The experimental data obtained also show that an increase in the H_2SeO_3 concentration (Fig. 5) or in the length of t_{imm} (Fig. 6) has a rather slight effect upon the height and position of the new current peak during the cathodic sweep. These factors exert a more marked effect upon the counterpeak.

DISCUSSION

The electrochemical behaviour of Se(IV) species irreversibly adsorbed onto platinum surface is well documented [15, 16, 18, 20, 41, 49]. Among the experimental features which have already been revealed, several facts relative to the problem to be investigated here deserve attention.

Firstly, from the chemistry of selenium [43], it was reasonable to assign the selenium surface redox process at $E < +1.0 \text{ V}$ to the reaction



(jointly with the formation of adsorbed Se(IV) species at higher positive E). So, it has been recognized that selenium irreversibly adsorbs onto platinum(hkl) by immersion in H_2SeO_3 or selenite solutions, and this adsorption leads to the formation of Se(0) adlayers which undergo a surface redox process involving 4 electrons, as was reported, e.g., in [41]. Then it may be assumed that the same selenium surface redox process is plausible for a polycrystalline Pt electrode as well.

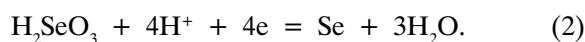
Secondly, when an arrangement of foreign atoms on various substrates has to be discussed, it is necessary to know the number of substrate sites occupied by a foreign adatom (S). Regarding platinum as a substrate and selenium as a foreign adatom, the parameter S was found to be equal to *ca.* 2 on polycrystalline platinum [49] and to 3 on Pt(111) [41].

Thirdly, considering the coverage of platinum by selenium adatoms, it should be noted that generally the structure of the selenium adlayer can be established in UHV or electrochemical environments. In particular, the structure of Se overlayer on Pt(111)

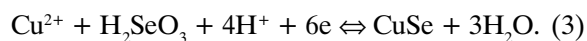
has been studied depending on selenium coverage under UHV conditions [50]. Although no data are available on electrochemical environments, it has been suggested [15] that this structure may be very similar. Then, the higher stable coverage in the latter environment will be 0.33, in which each Se atom blocks three platinum surface atoms [41], and the selenium adlayer on Pt(111) must correspond to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure [50]. Higher coverages can be achieved up to a value very close to 0.50 [15] (this value agrees well with the maximum θ_{sc} in UHV environments [50]). As can be seen, the experimental values of θ_{sc} obtained here are practically the same as those treated above.

Fourthly, considering the aim of our study, some comments on the coadsorption of Cu and Se on the polycrystalline Pt electrode seem to be necessary. The simultaneous electrochemical codeposition of Cu and Se from aqueous Cu(II) and Se(IV) solutions onto various substrates has already been investigated by several groups (see, *e.g.*, [18, 20]). A review of different works in this area has recently been presented in [51]. Based on an analysis of thermodynamic and experimental voltammetric data, these were aimed at understanding the mechanism of the formation and dissolution of binary and ternary selenides as separate phases.

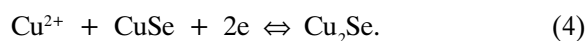
From the Pourbaix-like diagram for the Cu+Se+H₂O system at 25 °C, the following reactions have been predicted in the ranges of pH and E which were pertinent to the studies discussed above. In the pH range 0.5–1.5 and at E close to +0.70 V, a stable Se(IV) species, namely selenite, has been suggested to reduce to Se(0) [18]:



or, according to the considerations in [20], to Se(-II) in the presence of Cu²⁺:



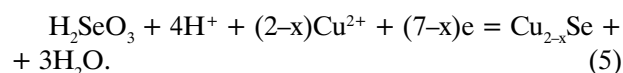
As the electrode potential is further decreased, the formation of Cu₂Se could be expected [20]:



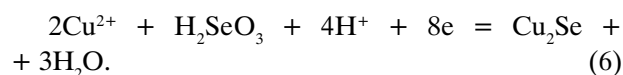
The reduction of CuSe to Cu₂Se with the negative shift of E has also been discussed in [18]. Both groups of authors have noted that formation of CuSe occurs at a more positive E than the reduction of Cu²⁺ to Cu. In relation to this note, it should be mentioned that a more general thermodynamic treat-

ment of such an “underpotential” formation of semiconductors has been presented in [52].

From the voltammetric data obtained in the binary Cu + Se system, it has been observed [18] that when Cu²⁺ and SeO₂ are present simultaneously, the reduction current starts at a more positive E than in the absence of either component. It has also been obtained that on the return scan no stripping peak of Cu(0) is observed, suggesting that Cu is present as Cu_{2-x}Se rather than as Cu(0) [18]. The formation of Cu_{2-x}Se has been proposed to occur according to the reaction [18]:



Investigations in this field have also been undertaken in [20]. The cathodic current peak at +0.35 V (0.1 M H₂SO₄ + 1·10⁻³ M Cu²⁺ + 2.4·10⁻⁴ M Se(IV), 10 mV s⁻¹, 1000 rev min⁻¹) has been assigned to the reaction:



Based upon an examination of the dependences of the height of this peak on the potential sweep rate, Se(IV) concentration and on the electrode rotation speed, it has been assumed [20] that the reaction (6) is not limited by a mass transport but rather by a surface process. The formation of Cu₂Se at the current peak mentioned has been characterized by energy-dispersive X-ray measurements jointly with scanning electron microscopy. Furthermore, it has also been supposed that PtSe active sites formed on a Pt electrode at E close to + 0.45 V induce Se(IV) reduction to Se(-II)_{ads} in acidic Se(IV) solution and that this should be the case in the presence of Cu²⁺ as well [20].

Quite apparently, the electrochemical measurements carried out earlier [18, 20] and those undertaken here are rather different as to the aims and experimental conditions. Among such differences, the deposition of the thicker films of Se compounds undertaken earlier and the formation of submono- or monolayers of selenium and copper in our study might be mentioned. Therefore, through a comparison of experimental data can provide a useful check, their interpretation is assumed to be dissimilar.

Now, let us turn to the voltammograms recorded here for the Se-modified Pt electrode in such an E range which is known [1–3, 7, 36–38, 44] to be associated with Cu UPD. It was obtained that the overall charge underneath the cathodic half-cycle cur-

ve (Fig. 2) was almost the same irrespective whether the bare Pt electrode or the Se-modified Pt electrode were applied in LSV experiments. Particularly, such a charge (corrected for double-layer charging) for the bare Pt (*cf.* Fig. 2a, curve 1) or the selenium-modified Pt (*cf.* Fig. 2c, curve 1) was found to be approximately equal to 1090 or 1010 μC , respectively. Then, taking into account the roughness factor $f \approx 2.35$, these quantities correspond to the charge densities of *ca.* 460 or 430 $\mu\text{C cm}^{-2}$, respectively. Both of these quantities are quite close to those expected for the formation of a complete zero valent Cu monolayer having the Pt lattice constant.

Considering that the amount of adsorbed selenium remains constant, *i.e.* Cu is not capable of displacing selenium from the Pt WE surface as pointed out above, the coadsorbed copper and selenium species should be assumed to exist. Then, one would expect that two possible adlayer structures might exist: either the segregated adlayers or the mixed ones. As in the cases of the selenium-modified Pt(111) electrode applied for Cu and formic acid oxidation [15, 16] or of the sulphur-modified polycrystalline Pt electrode used for Cu UPD [39], discrimination between the two possibilities from the voltammetric measurements only seems to be not possible.

However, some voltammetric features observed in our study suggest that the following interpretation is likely probable. Since selenium has a larger atomic radius than platinum (0.160 and 0.138 nm, respectively), part of platinum sites which have no selenium adspecies are still isolated with respect to copper (atomic radius of 0.128 nm) adsorption. Particularly, this may be the case at $\theta_{\text{Se}} \geq 0.3$, as a geometric room for Cu adatom to be deposited on Pt is formally insufficient. On the other hand, if it is assumed that selenium is not uniformly distributed on the platinum surface and that there is no strong lateral interaction between the selenium and copper adspecies, a certain variation in the compactness of selenium adlayer structure may occur. If this is the case, a certain part of copper adatoms may be deposited onto platinum at the beginning of the negative-going potential sweep; in other words, the formation of mixed selenium-copper adlayer onto platinum at a more positive E is believed to be possible. In our opinion, such a possibility can explain why a rather minor change in the i/E profile in the range of higher E is observed when the selenium-modified electrode is applied instead of bare platinum (*cf.* Figs. 5, 6b).

With the further negative E scan, when under the specific experimental conditions the newly formed current peak can be observed, the formation of bilayered structure, *i.e.* deposition of a separate copper layer on the selenium-covered platinum surface seems to be more reliable as a general trend. This should be possible assuming that the electron exchange between the surface and Cu^{2+} can occur through the relatively open selenium adlayer, as has been proposed for other systems, *e.g.*, for formic acid on arsenic- [53] or selenium- [15] modified Pt(111) electrodes.

In summary, in this work we have demonstrated that, using the selenium-modified polycrystalline Pt electrode in an acidic CuSO_4 solution, the specific pattern of the Cu UPD observed for a bare Pt electrode somewhat changed and a new current peak at potentials much closer to the bulk Cu deposition appeared. The model of copper deposition taking place on two active platinum surface domains, namely, on free Pt sites and on selenium-covered ones, was proposed. At present, such an interpretation of voltammetric data is given in a qualitative way only. Fuller examination on the Cu UPD onto the selenium-modified polycrystalline Pt is in progress.

CONCLUSIONS

A specific pattern of the Cu UPD characteristic of a bare polycrystalline Pt electrode somewhat changes and a new cathodic current peak at potentials much closer to the bulk copper deposition appears when a selenium-modified polycrystalline Pt electrode is applied in acidic CuSO_4 solution. This feature of the stabilized cyclic voltammograms is similar to that observed earlier for a sulphur-modified polycrystalline Pt electrode in an additive-free acidic CuSO_4 solution. A qualitative model of the Cu UPD taking place on two active platinum electrode surface domains, namely, on the free platinum sites in the range of higher potentials and on the selenium-covered ones at lower potentials corresponding to this new current peak was proposed.

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References

1. D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 11 (Eds. H. Gerischer and Ch. W. Tobias), p. 125, John Wiley & Sons, New York–Chichester–Brisbane–Toronto (1978).

2. H. Gerischer, D. M. Kolb and J. K. Sass, in *Advances in Physics*, **27**, 437 (1978).
3. R. R. Adžić, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 13 (Ed. H. Gerischer), p. 159, John Wiley & Sons, New York–Chichester–Brisbane–Toronto–Singapore (1984).
4. G. Kokkinidis, *J. Electroanal. Chem.*, **201**, 217 (1986).
5. K. Jüttner, *Electrochim. Acta*, **31**, 917 (1986).
6. O. A. Petrii and A. S. Lapa, in *Itogi Nauki i Tekhniki. Seriya-Elektrokhimiya*, Vol. 24 (Ed. Yu. M. Polukarov), p. 94, VINITI, Moscow (1987) (in Russian).
7. E. Budevski, G. Staikov and W. J. Lorenz, *Electrochemical Phase Formation and Growth*, VCH, Weinheim–New York–Basel–Cambridge–Tokyo (1996).
8. N. Furuya and S. Motoo, *J. Electroanal. Chem.*, **100**, 771 (1979).
9. M. Shibata and S. Motoo, *J. Electroanal. Chem.*, **187**, 151 (1985).
10. M. Shibata and S. Motoo, *J. Electroanal. Chem.*, **194**, 261 (1985).
11. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **194**, 275 (1985).
12. M. Shibata and S. Motoo, *J. Electroanal. Chem.*, **201**, 23 (1986).
13. M. Shibata and S. Motoo, *J. Electroanal. Chem.*, **229**, 385 (1987).
14. M. Shibata, O. Takahashi and S. Motoo, *J. Electroanal. Chem.*, **249**, 253 (1988).
15. M. J. Llorca, E. Herrero, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, **373**, 217 (1994).
16. E. Herrero, A. Rodes, J. M. Pérez, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.*, **412**, 165 (1996).
17. M. David, R. Modolo, M. Traore and O. Vittori, *Electrochim. Acta*, **31**, 851 (1986).
18. K. K. Mishra and K. Rajeshwar, *J. Electroanal. Chem.*, **271**, 279 (1989).
19. R. N. O'Brien and K. S. V. Santhanam, *J. Electroanal. Chem.*, **260**, 231 (1989).
20. P. Carbonnelle and L. Lamberts, *J. Electroanal. Chem.*, **340**, 53 (1992).
21. S. K. Haram, K. S. V. Santhanam, M. Neumann-Spallart, and C. Lévy-Clément, *Mat. Res. Bull.*, **27**, 1185 (1992).
22. L. Thouin, S. Rouquette-Sanchez and J. Vedel, *Electrochim. Acta*, **38**, 2387 (1993).
23. A. Garg, K. S. Balakrishnan and A. C. Rastogi, *J. Electrochem. Soc.*, **141**, 1566 (1994).
24. S. K. Haram and K. S. V. Santhanam, *J. Electroanal. Chem.*, **396**, 63 (1995).
25. R. N. Bhattacharya, A. M. Fernandez, M. A. Contreiras, J. Keane, A. Tennant, K. Ramanathan, J. R. Tuttle, R. N. Noufi and A. M. Hermann, *J. Electrochem. Soc.*, **143**, 854 (1996).
26. D. Lippkowitz and H.-H. Strehblow, *Electrochim. Acta*, **43**, 2131 (1998).
27. M. R. H. Hill and G. T. Rogers, *J. Electroanal. Chem.*, **68**, 149 (1976).
28. T. I. Lezhava, *Acceleration at Metal Deposition*, Diss., A. N. Frumkin Inst. Electrochem., Moscow (1989) (unpubl., in Russian).
29. E. Juzeliūnas, I. Kamuntavičienė, V. Katkutė and R. Sližys, *Trudy AN Lit. SSR. Ser. B.*, **2(153)**, 26 (1986) (in Russian).
30. D. Šimkūnaitė and A. Steponavičius, in *Investigations in the Field of Deposition of Metals*, p. 5, IChChT, Vilnius (1990) (in Russian).
31. D. Šimkūnaitė and A. Steponavičius, *Chemija (Vilnius)*, Nr. 1, 16 (1992) (in Russian).
32. A. Steponavičius, D. Šimkūnaitė and V. Jasulaitienė, *Chemija (Vilnius)*, Nr. 2, 64 (1997).
33. A. Steponavičius, D. Šimkūnaitė and A. Survilienė, *Chemija (Vilnius)*, Nr. 3, 36 (1997).
34. A. Steponavičius, D. Šimkūnaitė and V. Kapočius, *Chemija (Vilnius)*, Nr. 4, 40 (1997).
35. A. Steponavičius, in *Abstracts of 40th Meeting of the Poland Chemical Society and the Poland Society of Engineers and Technicians of Chemical Industry*, Abstr. No. S-XIII, W-8, Gdańsk (1997).
36. V. Karpavičienė, V. Kapočius and A. Steponavičius, *Chemija (Vilnius)*, Nr. 4, 31 (1997).
37. A. Steponavičius and V. Kapočius, in *Abstracts of the 1997 Joint International Meeting of The Electrochemical Society and The International Society of Electrochemistry*, Abstr. No. 470, Paris (1997).
38. A. Steponavičius and D. Šimkūnaitė, *Chemija (Vilnius)*, Nr. 4, 297 (1998).
39. A. Steponavičius, S. Lichušina and D. Šimkūnaitė, *Chemija (Vilnius)*, **11** (4) 182 (2000).
40. T. Biegler, D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, **29**, 269 (1971).
41. J. M. Feliu, R. Gómez, M. J. Llorca and A. Aldaz, *Surf. Sci.*, **289**, 152 (1993).
42. H. Angerstein-Kozłowska, B. E. Conway, B. Barnett and J. Mozota, *J. Electroanal. Chem.*, **100**, 417 (1979).
43. S. I. Zhdanov, in *Encyclopedia of Electrochemistry of the Elements*, Vol. IV (Ed. A. J. Bard), Chapt. IV-7, Marcel Dekker, Inc., New York–Basel (1975).
44. D. Margheritis, R. C. Salvarezza, M. C. Giordano and A. J. Arvia, *J. Electroanal. Chem.*, **229**, 327 (1987).
45. A. Steponavičius and S. Lichušina, *Chemija (Vilnius)*, **10**, Nr. 1, 36 (1999).
46. D. P. Bhatt, T. Twomey, W. Plieth, R. Schumacher and H. Meyer, *J. Electroanal. Chem.*, **322**, 279 (1992).
47. J. H. White and H. D. Abruña, *J. Electroanal. Chem.*, **300**, 521 (1991).
48. E. Schmidt and S. Stucki, *J. Electroanal. Chem.*, **39**, 63 (1972).
49. N. Furuya and S. Motoo, *J. Electroanal. Chem.*, **98**, 189 (1979).
50. M. P. Kiskinova, A. SzabŃ and J. T. Yates, Jr., *Surf. Sci.*, **226**, 237 (1990).
51. R. P. Pandey, S. N. Sahu and S. Chandra, *Handbook of Semiconductor Electrodeposition*, Chaps. 7 and 8, Marcel Dekker, Inc., New York–Basel–Hong Kong (1996).
52. F. A. Kröger, *J. Electrochem. Soc.*, **125**, 2028 (1978).
53. A. Fernandez-Vega, J. M. Feliu, A. Aldaz and J. Clavilier, *J. Electroanal. Chem.*, **305**, 229 (1991).

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KAI KURIŲ PRIEDŲ ĮTAKA Cu SLUOKSNIŲ FORMAVIMUISI POTENCIALŲ ZONOSE, TEIGIAMESNĖSE IR NEIGIAMESNĖSE UŽ PUSIAUSVYRINĘ Cu^{2+}/Cu SISTEMOS POTENCIALO REIKŠMĘ, RŪGŠČIUOSE $CuSO_4$ TIRPALUOSE. 6. PRIEŠVOLTAŽINIS Cu NUSODINIMAS ANT POLIKRISTALINĖS Pt ELEKTRODO, MODIFIKUOTO CHEMOSORBUOTU Se

S a n t r a u k a

Priešvoltažinis Cu nusodinimas (UPD) ant seleno modifikuoto polikristalinės Pt elektrodo rūgščiame $CuSO_4$ tirpale buvo tiriamas naudojant ciklinę voltamperometriją. Parodyta, kad Cu UPD ant grynos Pt procesui būdinga ciklinės voltamperogramos (CVA) forma išnyksta, bet atsiranda naujas srovės maksimumas, kuris yra kur kas arčiau prie tūrinio Cu nusodinimo zonos. Toks CVA bruožas jau buvo pastebėtas anksčiau, kai Cu buvo nusodinamas ant švaraus Pt elektrodo iš selenito turinčių rūgščių $CuSO_4$ tirpalų arba ant siera modifikuoto Pt elektrodo iš $CuSO_4$ tirpalų be priedų. Pasiūlytas Cu nusodinimo modelis, kuriame atsižvelgta į tai, kad metalas gali būti nusodinamas ant dviejų aktyvių Pt paviršiaus vietų – ant laisvojo Pt paviršiaus ir ant adsorbuotu seleno apdengto paviršiaus.

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ВЛИЯНИЕ НЕКОТОРЫХ ДОБАВОК НА ФОРМИРОВАНИЕ Cu СЛОЕВ В ЗОНАХ НЕДОНАПРЯЖЕНИЯ И ПЕРЕНАПРЯЖЕНИЯ В КИСЛЫХ $CuSO_4$ РАСТВОРАХ 6. ОСАЖДЕНИЕ Cu В ЗОНЕ НЕДОНАПРЯЖЕНИЯ НА ПОЛИКРИСТАЛЛИЧЕСКОМ Pt ЭЛЕКТРОДЕ, МОДИФИЦИРОВАННОМ ХЕМИСОРБИРОВАННЫМ Se

Р е з ю м е

Осаждение Cu в зоне недонапряжений на гладкой поликристаллической Pt, модифицированной селеном, в кислом $CuSO_4$ растворе исследовалось с использованием циклической вольтамперометрии. Специфический ход циклических вольтаммограм (ЦВА), наблюдаемый для чистой Pt, исчезает, но появляется новый пик при потенциалах, намного ближе к зоне осаждения фазовой Cu. Такое свойство ЦВА уже наблюдалось ранее, когда осаждение Cu проводилось на чистой Pt из кислых $CuSO_4$ растворов, содержащих селенит, или на Pt электроде, модифицированном серой, из $CuSO_4$ растворов в отсутствие добавок. Предложена модель осаждения Cu, в которой учитывается возможность осаждения металла на двух активных участках Pt поверхности – на чистой Pt и на Pt поверхности, покрытой адсорбированным селеном.